Acta Chemica Scandinavica, 1995: 49: 800–802
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

An Electron Diffraction Study of Co_3Sn_2

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Larsson, A.-K., Stenberg, L. and Lidin, S., 1995. An Electron Diffraction Study of Co_3Sn_2. – Acta Chem. Scand. 49: 800–802 © Acta Chemica Scandinavica 1995.

Electron diffraction on single domains of the γ′-Co_3Sn_2 phase unambiguously confirms an orthorhombic supercell. The reciprocal lattice can be indexed using $\boldsymbol{G} \pm m\boldsymbol{q}$, where $\boldsymbol{G}$ refers to the Bragg reflections of a NiAs (B8)-type lattice ($P6_3/mmc$) and $\boldsymbol{q} = \boldsymbol{a}^*/4 + \boldsymbol{b}^*/4$ is the modulation vector. Other modulations of the base lattice occur in the γ-Co_3Sn_2 region.

This work is part of a project on intermetallic T-B phases focused on structures where T is one or several first-row transition metals and B is tin.

A large number of intermetallic phases crystallize in the NiAs($B8_1$) structure type ($P6_3/mmc$, B in Wyckoff position 2c and T in 2a). Villars[1] lists 241. The larger, more electronegative, atom B forms a hexagonal close-packed array and T are in all octahedral interstities. The structure contains trigonal bipyramidal voids which may be filled to yield another common structure type, that of Ni_2In ($B8_2$), often referred to as 'stuffed' NiAs (Villars[1] lists 154). Partial occupancy of the trigonal bipyramids may either result in a disordered intermediate with partial occupancies, or in ordered super structures. γ′-Co_3Sn_2 is an example of such an ordered structure, and γ-Co_3Sn_2 was previously reported as a disordered structure. The coordination polyhedron around the additional Co atom is an 11 polyhedron consisting of the five Sn atoms from the hexagonal closepacked array and six Co atoms from the centres of the octahedra. This polyhedron is referred to as an Edshammar polyhedron.[2–4]

Nial[5] noticed that γ-Co_3Sn_2 undergoes a phase transformation to a superstructure, γ′-Co_3Sn_2, when cooled below 550°C. The X-ray diffraction patterns obtained could be indexed in a hexagonal cell ($a_{hs} = 4a_h$, $c_{hs} = c_h$) or an orthorhombic cell ($a_o = 2a_h$, $b_o = a_h + 2b_h$, $c_o = c_h$). No single crystals suitable for single-crystal X-ray work were obtainable to confirm either cell.

Brand[6] favoured an orthorhombic description of the supposedly isotypic γ′-Ni_3Sn_2 based on shielded Weissenberg photographs from a specimen containing crystallites of three different domain orientations, with the hexagonal c-axis in common. In his description zig-zag rows of Ni-filled and empty trigonal bipyramids alternate to give the structure in Fig. 1. Rajeswari[7] demonstrated that γ′-Co_3Sn_2 is isostructural to γ′-Ni_3Sn_2 by employing Brand's method of shielded Weissenberg photographs. The cell dimensions for γ′-Co_3Sn_2 obtained by him show strong orthorhombic distortion with respect to the hexagonal NiAs subcell. This is in disagreement with the findings of Nial.[5] Jain *et al.*[8] further emphasized the orthorhombic super-cell and the excellent agreement between the parameters for the sub-cell and those for the super-cell, while Panteleimonov *et al.*[9] favoured a hexagonal description. Fjellvåg and Kjekshus[10] supported Brand's model of the γ′-Co_3Sn_2 structure by refining powder data with the Rietveld method.

In the present investigation we unambiguously confirm the correctness of the orthorhombic structure by means of single-domain electron diffraction. We show that the dimensions of the base cell do not deviate from hexagonal symmetry within the detection limits of electron diffraction for crystals grown by slow cooling from 1100°C to room temperature (50°C h^{-1}). Additionally a new modulation of the high-temperature form, γ-Co_3Sn_2, was detected.

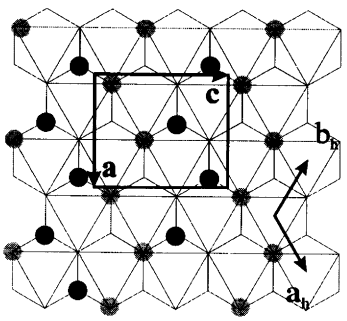

Fig. 1. The crystal structure of γ′-Co_3Sn_2 projected along $\boldsymbol{b}(=\boldsymbol{c}_h)$. The hcp array consists of Sn atoms, while the octahedra are filled with Co. Co in the trigonal bipyramids are drawn as black and grey spheres at $z = 1/4$ and 3/4, respectively.

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The Co_3Sn_2 γ'-phase

In the γ'-Co_3Sn_2 structure, half of the available trigonal bipyramids are occupied by Co atoms. Alternating rows of filled and empty polyhedra form zigzag chains along the *a*-axis Brand[6] yielding a unit cell in spacegroup *Pnma*, with $\boldsymbol{a} = \boldsymbol{a}_h - \boldsymbol{b}_h$, $\boldsymbol{b} = \boldsymbol{c}_h$ and $\boldsymbol{c} = 2\boldsymbol{a}_h + 2\boldsymbol{b}_h$, cf. Fig. 1. Macroscopic crystals are domain-twinned, but with selected area electron diffraction it is possible to record electron diffraction from one single domain (Figs. 2a and 2b). In Figs. 2c and 2d the electron diffraction originates from two domains, and in Figs. 2e and 2f from three domains. Figures 2c–2f show the superpositions of two or three copies of the principal reciprocal lattice (without systematic extinctions) rotated by $2\pi/3$ relative to each other and corresponding electron diffractions patterns. The additional diffraction spots in the experimental electron diffraction (ED) pattern of all three domains (Fig. 2f) are due to dynamical diffraction between different domains. This is due to the perfect alignment between the

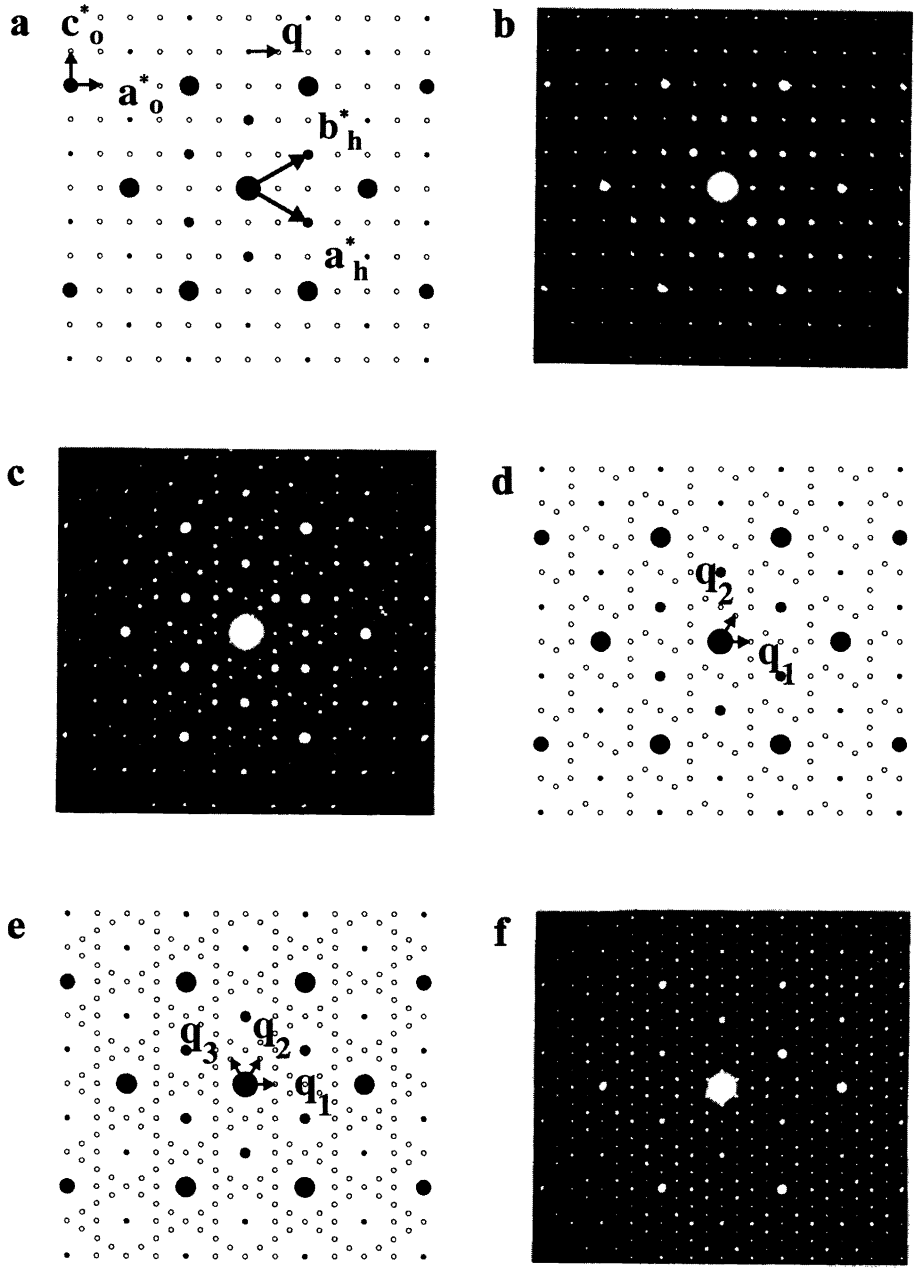

Fig. 2. Electron diffraction (ED) patterns and principle reciprocal lattices of γ'-Co_3Sn_2 along [010] (=$[001]_h$). The reciprocal cells of the NiAs-type base cell and of the orthorhombic supercell are marked as is the modulation vector $\boldsymbol{q}$, of the base lattice. (a,b) One domain; (c,d) two domains; (e,f) three domains.

domains, caused by the CoSn-sublattice being common to all domains in the grain. The perfect hexagonal base matrix of the ED pattern confirms Jain's[8] results.

In our study, ED patterns from different crystals, and different parts of these crystals, display a variety of intensity distributions due to the amount of each crystallographic orientation present. The one-domain parts are only found at edges of very thin crystals. The domains are hence very thin, roughly estimated as ca. 100 Å. Since twinning occurs both along the hexagonal *c*-axis and perpendicular to it (sandwich twinning), sizes are hard to estimate.

After further and more intense beam irradiation some of the superstructure reflections weaken. After some time these disappear altogether. The resulting diffraction pattern is shown in Fig. 3. This diffraction pattern could be explained by the superposition of three diffraction patterns from three domains, as above, but with only the first modulation of the superstructure discernable ($\boldsymbol{q} \approx \boldsymbol{a}_h^*/4 + \boldsymbol{b}_h^*/4$). The modulation vector deviates slightly (up till about 2%) from the commensurate case. The structural origin of this ED pattern is not clear. Destruction of the order in the Co arrangement is one explanation. This would cause the higher-order modulations to decrease in intensity before the phase is totally disordered (with respect to the cobalt in the Edshammar positions). The phase reverts to the simple hexagonal NiAs subcell on further irradiation, suggesting the complete disordering atoms in the γ-phase. Because of the crude way of initiating the phase transitions, no definite data concerning the intermediate phase could be given.

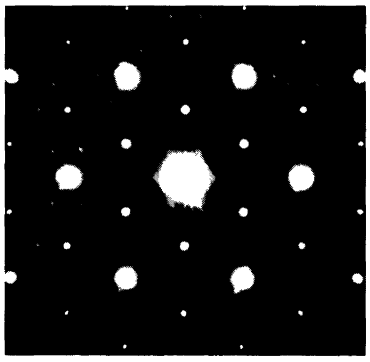

Fig. 3. Electron diffraction recorded after electron beam treatment of the γ'-Co_3Sn_2 phase (cf. Fig. 2 for indexing). Only the first harmonic of the modulation of the superstructure lattice ($m=1$ in $\boldsymbol{G} \pm m\boldsymbol{q}$) is visible.

Attempts to synthesise this phase directly (annealed at 1100°C and quenched) revealed further modulations in the γ'-Co_3Sn_2 region. One modulation with diffuse scattering and at least one additional superstructure have been detected. The area in the phase diagram needs to be carefully scanned as a function of temperature and composition to reveal all modulations and their relations.

Conclusions

The domain character of γ'-Co_3Sn_2 was investigated. The domains are small and the base lattice is not distorted with respect to the perfect hexagonal lattice. The dimensions of the orthorhombic unit cell follow exactly $c = a \sin \pi/3$. In the electron diffraction patterns there is no evidence for splitting of the (210)–(020) reflections, which would be separated if the unit cell were distorted: this despite the fact that the atoms are shifted significantly with respect to the hexagonal symmetry.

This phase is not the only superstructure of the γ-region of the Co–Sn phase diagram. The area needs to be carefully investigated (by electron diffraction) as a function of temperature and composition to reveal all different modifications and their structural relations.

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Received November 20, 1994.